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Structural and microwave properties of (Ba, Sr)TiO_3 films grown by pulsed laser deposition

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Abstract. The relationship between the structure and the microwave dielectric properties of epitaxial $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) films has been investigated. Single-phase BST films (40–160 nm) have been deposited onto (100) MgO substrates by pulsed laser deposition. As-deposited films show a significant tetragonal distortion. The in-plane lattice parameters (a) are always larger than the surface normal lattice parameters (c). The tetragonal distortion depends on the thickness of the films and the post-deposition annealing conditions. Films annealed at 900 °C show less tetragonal distortion than the as-deposited film and the films annealed at higher temperatures. The distortion in the film is due to stress caused by the lattice mismatch and thermal expansion coefficient differences between the film and the substrate. The dielectric constant and its change with dc bias voltage of BST films on MgO at microwave frequencies increase with increasing annealing temperature from 900 °C to 1200 °C, which corresponds to an increase in the tetragonal distortion.

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Thin films of $Ba_xSr_{1-x}TiO_3$ (BST) are being developed for tunable microwave device applications, such as filters, phase shifters, and delay lines, due to the fact that the materials exhibit a large dielectric constant change with dc bias voltage [1–3]. BST thin films have been grown by several methods, such as sputtering, evaporation, MOCVD, MOVPE, MBE, pulsed laser deposition (PLD) [4]. PLD provides unique advantages for oxide film growth, because it easily reproduces the stoichiometry of the target in multicomponent oxide materials. PLD-grown BST films have shown good characteristics for tunable microwave applications with a low loss tangent ($\tan\delta < 0.01$) and a large dielectric constant change ($\approx 60\%$ with 67 kV/cm dc bias field) at 1–20 GHz [1, 2]. In this paper, the relationship between film stress and the microwave dielectric properties of epitaxial BST films on (001) MgO has been investigated as a function of the thickness and the post-deposition annealing conditions.

The dielectric properties measured at microwave frequencies for BST films are affected by many factors, such as substrate type, film thickness, grain size, dopant type, Ba/Sr or Ti/(Ba + Sr) ratio, and film stress [3, 5, 6]. In particular, the stress effect has been studied by Abe et al. [7], and Chang et al. [2]. In BST films deposited by PLD on MgO, the dielectric constant and the dielectric loss tangent decrease after a post-deposition anneal at temperatures < 1000 °C in oxygen flow for 6 h [2]. This result was attributed to the filling of oxygen vacancies and the changes in film stress, which may affect the extent of ionic polarization.

Stress in the epitaxially grown BST films on MgO can be estimated from measuring the lattice parameters of the film along surface normal (c) and in-plane (a) directions. The stress comes from two major sources; lattice mismatch and thermal expansion differences between the film and the substrate [9, 10]. Biaxial stress (S), which is positive for tensile stress, in the plane of the film due to the lattice mismatch between the substrate and the film can be calculated from measured film lattice parameters (a and c) as follows:

$$S = \frac{E_f}{1-\upsilon_f}\left(\frac{a-a_o}{a_o}\right) = \frac{E_f}{2\upsilon_f}\left(\frac{a_o-c}{a_o}\right), \quad (1)$$

where E_f is Young's modulus of the film, $\upsilon_f = C_{12}/(C_{11}+C_{12})$ is Poisson ratio of the film, Cs are matrix components of the elastic stiffness constants of the film, and a_o is the cubic lattice parameter of the unstrained film or bulk. Stress due to the thermal expansion difference between the film and the substrate can be expressed by

$$S = (\alpha_f - \alpha_s)\Delta T E_f, \quad (2)$$

where α_f and α_s are the thermal expansion coefficients of the film and the substrate, respectively, and ΔT is the temperature difference between the growth (750 °C) and the measurement (room temperature).

1 Experiment

BST films were deposited onto (100) MgO single crystals by PLD. A short-pulse excimer laser (248 nm, 30 ns FWHM) was focused on the rotating BST target with energy density of

$2\,J/cm^2$ in flowing O_2 at a pressure of 350 mTorr. Three BST films with different thicknesses (40, 80, and 160 nm) were deposited at a substrate temperature of 750 °C. Pieces of each sample were placed inside of a BST vessel, then annealed at three different temperatures (900, 1100, and 1200 °C) for 6 h in flowing O_2 [1]. Microwave properties of the BST films at 1–20 GHz range were measured by HP 8510C network analyzer using interdigitated capacitors fabricated from depositing Ag electrodes with a thin Au layer by e-beam evaporation through a PMMA lift-off mask [8].

The lattice parameters of BST films were measured using a Rigaku rotating anode X-ray diffractometer using Cu $K\alpha$ radiation. For epitaxial films on (001) MgO substrate, the diffraction peaks observed by a conventional $\theta - 2\theta$ scan ((002) and (004)) only provides structural information related to the lattice parameter along the film surface normal direction (c). To obtain in-plane information, asymmetric X-ray diffraction peaks with mixed h, k, l indices, such as (024) and (113), were measured. The diffraction peak of the MgO substrate was used as an internal standard. In addition, each BST diffraction peak was fitted with two Gaussian functions, corresponding to Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations, after removing the background. The lattice parameters of the BST films are calculated by the least-square method with four BST peaks, (002), (004), (113), and (024). The uncertainty of the lattice parameter along surface normal direction (c) is of the order of 0.001 Å, whereas that along in-plane (a) is in the range between 0.001–0.006 Å.

2 Results and discussion

Typical symmetric (004) and asymmetric (024) X-ray diffraction peaks of BST on MgO are shown in Fig. 1a and b, respectively. The diffraction patterns shown in Fig. 1 were taken from films with 160 nm in thickness as a function of the post-deposition annealing conditions (as-deposited and 900–1200 °C). The peak position of (004) BST remained the same as shown in Fig. 1a, whereas the position of the (024) reflection, Fig. 1b, shifted as a function of annealing conditions.

Figure 2a shows the dependence of the lattice parameters along the in-plane, a, and the surface normal direction, c, as a function of film thicknesses and annealing temperatures. The lattice parameters along the surface normal show less

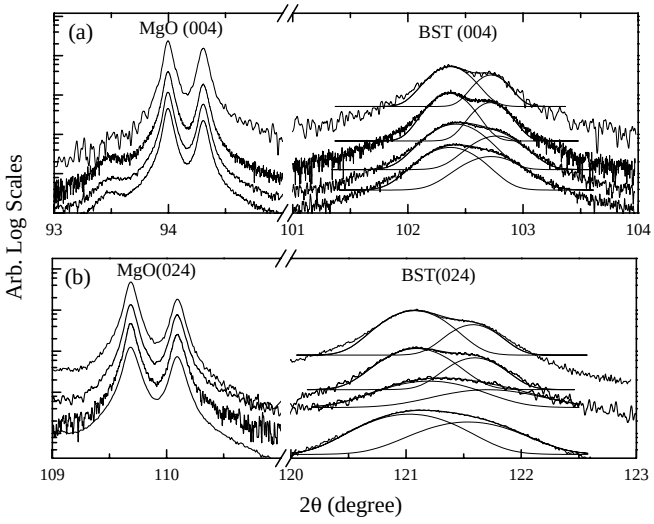

Fig. 1a,b. (004) (**a**) and (024) (**b**) X-ray diffraction patterns of 160-nm-thick BST film on (001) MgO with different post-deposition treatment from bottom to top, as-deposited and 900, 1100, and 1200 °C annealing for 6 h, respectively. *Thin solid lines* correspond to the $K\alpha_1$ and $K\alpha_2$ peaks

variation than those along the in-plane direction. In addition, the lattice parameters along the surface normal are always smaller than those along the in-plane direction ($a > c$). The tetragonal distortion ratio (a/c) is shown in Fig. 2b. The as-deposited thick films (80–160 nm) have similar distortions, whereas that of thin film (40 nm) has less distortion and is close to the bulk value. After the annealing, we observed two different types of behavior in the tetragonal distortion of films of different thicknesses. The thin film annealed at 900 °C shows more distortion than the as-deposited film, and the distortion decreases with increasing annealing temperature. The distortion measured in the two thick films is decreased when the film is annealed at 900 °C. However, the distortion increases again with increasing annealing temperature.

Stress in the film due to the thermal expansion coefficient difference between film and substrate can be estimated from (2). The thermal expansion coefficients of the BST film (α_f) and MgO substrate (α_s) are 10.5×10^{-6} /°C, and 13.8×10^{-6} /°C, respectively [4]. Though these numbers are temperature-dependent variables, it is still reasonable to estimate that the thermal expansion coefficient of the BST is smaller than that of MgO. The temperature difference be-

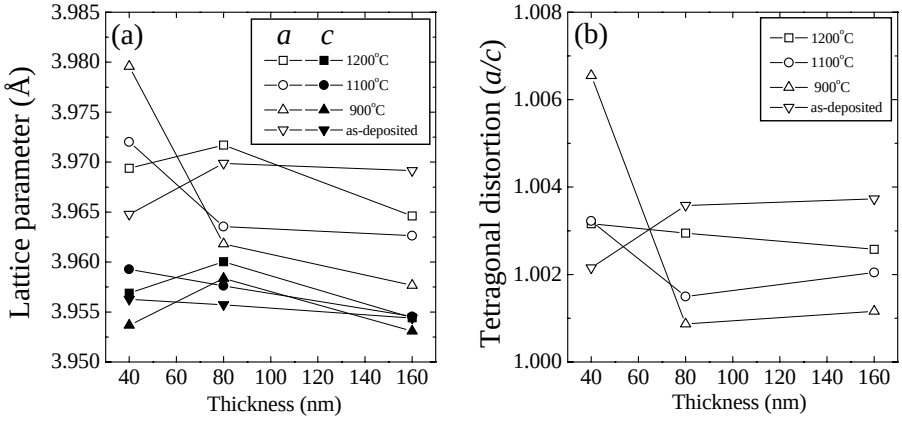

Fig. 2a,b. Lattice parameters along in-plane and surface normal directions (**a**), and tetragonal distortion ratios (a/c) (**b**) of BST films on MgO with different thickness and different annealing temperature

Table 1. Thermal expansion coefficient, equilibrium lattice parameter at room temperature, calculated lattice parameter at 750 °C, expected in-plane lattice parameters of BST on MgO with two extreme cases, following thermal contraction of MgO for thin film and BST for thick film, and measured in-plane lattice parameters of thin and thick films

	Thermal expansion coef. (10^{-6}/°C)	20 °C	750 °C	750 °C → 20 °C	Measured in-plane lattice parameter
MgO	13.8	4.2110 Å	4.2525 Å	4.2525 Å → 4.2110 Å	
BST	10.5	3.9606 Å	3.9909 Å	4.0000 Å → 3.9610 Å (thin film) → 3.9695 Å (thick film)	3.9648 Å (40-nm film) 3.9695 Å (80–160 nm film)

tween the growth and measurement (ΔT) for this experiment was 730 °C. This calculation yields negative stress, indicating compressive stress by definition of biaxial stress, whereas actual measurement suggests that the films are under tensile stress because the in-plane lattice parameter a is larger than that of the surface normal c. This may suggest that the compressive stress of the film is suppressed by other tensile stress such as lattice mismatch stress.

From (1), we can derive a relationship between in-plane and surface normal lattice parameters:

$$a = \{(1 + v_f)/2v_f\}a_o - \{(1 - v_f)/2v_f\}c \,. \quad (3)$$

The Poisson ratio, $v_f = 0.3082$, for $Ba_{0.5}Sr_{0.5}TiO_3$ was estimated from elastic stiffness constants of $SrTiO_3$ and $BaTiO_3$ [11]. Typically, the lattice parameter of the bulk material is used for this kind of calculation for semiconductors and perovskites [9, 12, 13]. However, using the known lattice parameter of bulk $Ba_{0.5}Sr_{0.5}TiO_3$, $a_o = 3.9471$ Å [14], with the measured $c = 3.9544$ Å yields a smaller in-plane lattice parameter, $a = 3.938$ Å, than the measured in-plane value, 3.9691 Å, which suggests that the lattice parameter of an unstrained BST film is different from that of bulk. Oxide films grown by PLD in low partial pressure of O_2 tend to have a larger lattice parameter than that of the bulk, because of oxygen deficiency which leads to an increase the lattice parameter of the perovskite [15, 16].

A stress-free BST film was obtained using a two-step process. First, a thin layer of BST (50 nm) is deposited at room temperature followed by the deposition of the same material at high temperature (750 °C). The deposited film shows an X-ray diffraction pattern consistent with a poly-crystalline single-phase film. This structure was confirmed by TEM. The measured lattice parameter (a_o) of the unstrained BST film is 3.9606 Å as determined by X-ray diffraction. This poly-crystalline film could be considered as a new equilibrium state with the given O_2 partial pressure (350 mTorr) at deposition temperature (750 °C) and a stress-free film due to absence of preferential orientation. The in-plane lattice parameter ($a = 3.968$ Å) of the epitaxial BST film was obtained by calculating (3) with the poly-crystalline lattice parameter ($a_o = 3.9606$ Å). The difference between the measured (3.969 Å) and calculated (3.968 Å) in-plane lattice parameter is less than 0.03%. This agreement suggests that the lattice parameter for the poly-crystalline film can be used in the stress calculation as an unstrained film.

The lattice parameter of BST ($a_{RT} = 3.9606$ Å unstrained film) and bulk MgO ($a = 4.2110$ Å) will expand according to the thermal expansion coefficient as shown in Table 1. Though the calculated lattice parameter of BST is 3.9905 Å at the deposition temperature (750 °C), the in-plane lattice parameter of BST on MgO increases due to larger MgO lattice. During cooling of the sample to room temperature, the in-plane lattice of a thin BST film should follow the contraction of the MgO substrate, while that of a thicker film may follow the contraction of the bulk BST. As the thickness of the BST films increases, the effect of the MgO substrate on the film during cooling is less dominant. An estimated in-plane lattice parameter (4.0000 Å) of BST at 750 °C will contract to two different in-plane lattice parameters at room temperature depending on the thickness of the BST film (3.9610 Å for thin film and 3.9695 Å for thick film contracting with MgO and BST thermal properties, respectively). These estimated in-plane lattice parameters are comparable to measured ones (3.9648 Å for thin and 3.9695 Å for thick films, respectively).

Annealing films in an oxygen environment will reduce the unit cell size of the BST films by lattice relaxation and filling oxygen vacancies. This was observed for thicker films

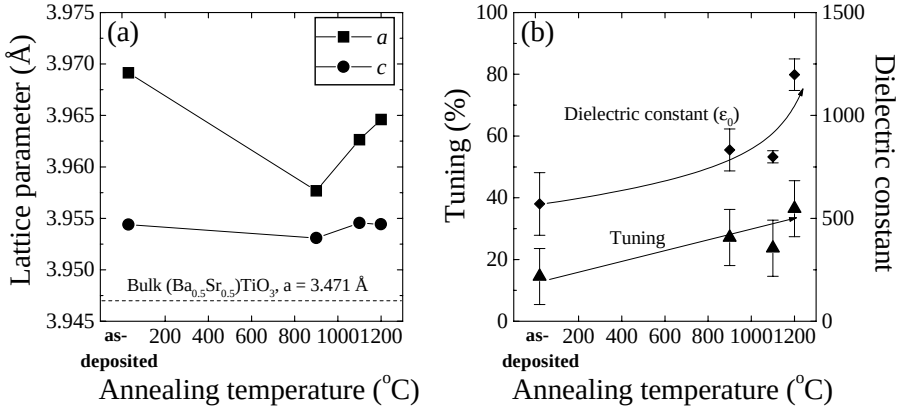

Fig. 3a,b. Lattice parameters (**a**) and zero field dielectric constants (ε_0) and % tuning (**b**) of BST film (160 nm) on MgO at 10 GHz with different post-deposition annealing conditions (as-deposited, and annealing at 900, 1100, and 1200 °C)

(80–160 nm), whereas the thin film shows opposite behavior (an increase in in-plane lattice parameter). This indicates that thin films are more constrained by the substrate than thicker films.

The lattice parameters, zero-field dielectric constant (ε_0) and % tuning measured at 10 GHz are shown in Fig. 3 for the different annealing conditions for the 160-nm-thick BST films. The % tuning was defined as $100(\varepsilon_0 - \varepsilon_{dc})/\varepsilon_0$, where ε_0 and ε_{dc} are dielectric constants with 0 and 80 kV/cm applied dc bias field on the interdigitated capacitor, respectively. The dielectric constant and % tuning increase after post-deposition annealing. The dielectric constant of the annealed films increases with increasing tetragonal distortions and increasing annealing temperatures. This result indicates that the larger in-plane lattice parameter may lead to larger polarizability resulting in a larger dielectric constant.

3 Summary

The in-plane lattice parameters of epitaxial BST thin films on MgO grown by PLD are always larger than those of the surface normal direction for all thickness (40–160 nm) and all post-deposition conditions (as-deposited, annealing at 900–1200 °C). This result suggests that the BST film on MgO is in tensile stress. Thick annealed films (80–160 nm) show a reduced tetragonal distortion compared to as-deposited films. Further, the tetragonal distortion of annealed thick films is reduced with decreasing annealing temperature, whereas that of thin film (40 nm) is increased. This result indicates that the stress in the film depends on the film thickness. In a thin film the stress is dominated by the MgO thermal contraction, while for thicker films the stress is determined by bulk BST thermal contraction. Assuming the polycrystalline film is stress free, the calculated in-plane lattice parameter of epitaxially grown BST film on MgO is in agreement with that of actual measurement within 0.03%. The dielectric constant of BST films on MgO single crystals at 10 GHz increases after a post-deposition anneal. For annealing temperatures above 900 °C, the dielectric constant of the annealed films increases with increasing tetragonal distortion. This result indicates that the larger in-plane lattice parameter provides the larger ionic displacement along in-plane direction, resulting in a larger dielectric constant.

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